Appendix A-1

Hydrogen through the Nineteenth Century

Man became aware of hydrogen as a flammable gas when he began mixing iron and sulfuric acid near a flame, an event that could have occurred as early as the eighth century and certainly no later than the sixteenth.= The use of hydrogen became such an integral part of the history of chemistry from the seventeenth through the nineteenth century that only selected highlights, covering properties pertinent to its use as a fuel, will be briefly summarized here.

Gaseous Hydrogen

Robert Boyle, one of the founders of modern chemistry, published the first description of the flammability of hydrogen in 1673 and Henry Cavendish described its flammability limits in air in 1766.÷ Cavendish's results were close to the modern limits of 4 to 75 percent hydrogen by volume. In contrast, the limits for gasoline vapor are 1 to 7 percent and for natural gas, 4 to 15 percent by volume. The very wide flammability limits of hydrogen make it easy to burn over a wide range of conditions, a great asset in a fuel. The same property, however, makes hydrogen hazardous to handle.

Cavendish, who called hydrogen "inflammable air," was also the first to measure its density. He reported in his 1766 paper that hydrogen is 7 to 11 times lighter than air (the modern value is 14.4). Cavendish's results not only opened up a new chapter in the history of gases, but also attracted attention to hydrogen as an alternate to hot air as a buoyant gas. Jacques Charles was first to take advantage of this soon after the first public demonstration of a hot-air balloon. After four days of struggling with his iron-acid hydrogen generation equipment, Charles launched his 4-meter balloon on 27 August 1783. Just over three months later, he and one of his balloon builders, Aine Robert, became the first men to ascend in a hydrogen balloon.×

With all the enthusiasm over ballooning that began with the Mongolfier brothers and Charles in 1783, it was inevitable that the good and bad properties of hydrogen would meet. The worst happened on 15 June 1785 when Pliatre de Rozier and an assistant, P. A. Ronaon, attempted to cross the English channel in a hydrogen balloon carrying a small hot-air balloon for altitude control. Thirty minutes into the flight the

hydrogen ignited and the two men perished. Hydrogen's flammability was the underlying cause of the first air tragedy.[4] Nevertheless, the attractiveness of hydrogen as a readily available buoyant gas was to outweigh the danger of flammability for 150 years of lighter-than-air flight. This application of hydrogen is the reverse of hydrogen's later role as a fuel, where its flammability is a major advantage and its low density the disadvantage that inhibits its use for flight in the atmosphere.

The increased demand for hydrogen for balloon flight following Charles's successes brought an early improvement in the technology of its generation. Although iron and sulfuric acid were readily available, their use in generating hydrogen was difficult to apply in the filling of balloons. In the winter of 1783–1784, a scientist and an inventor collaborated to bring a great improvement in hydrogen generation. The great French chemist, Antoine Lavoisier, and Charles Meusnier, army officer and inventor, generated hydrogen by passing steam through the red-hot barrel of an iron cannon. The Lavoisier-Meusnier process, with refinements, became the most effective and economical way to obtain hydrogen during the first part of the nineteenth century. Although still in use, the steam-iron method was largely replaced at the start of the twentieth century by two other methods: passing superheated steam over incandescent coke and electrolysis of a dilute solution of caustic soda.[5]

For use as a fuel, a property of hydrogen that is of even greater importance than flammability is the large amount of energy released during combustion. Lavoisier and Pierre Laplace measured the heat of combustion of hydrogen in 1783–1784 using an ice calorimeter. The experiment took 11½ hours and the amount of ice melted was equivalent to about $97 \cdot 10^6$ joules per kilogram of hydrogen. This was much higher than values obtained for other substances, and whether for this reason or other uncertainties, the results were not published until 1793. During the nineteenth century, the heat of combustion was measured many times. The modern value is $120 \cdot 10^6$ J/kg for gaseous reactants to gaseous products, so the Lavoisier-Laplace value was not too far off. In comparison, the heat of combustion of gasoline is $48 \cdot 10^6$ J/kg, less than half that of hydrogen.[6]

The density of gaseous hydrogen is so low that its heat of combustion on a volume basis does not compare favorably with denser fuels. Hydrogen was used in heating torches, but has largely been replaced by acetylene. Gaseous hydrogen was used in 1820 as fuel for one of the earliest internal combustion engines, but it was quickly replaced by coal gas which was much more readily available and had a higher heating value per unit volume.[7]

During the nineteenth century, other hydrogen properties, useful in fuel applications, were determined. The explosive limits of hydrogen-oxygen mixtures were found to be from 5.5 to 95 percent hydrogen by volume—much wider than its limits in air. The flame temperature of two parts hydrogen and one of oxygen was measured as 3117 K in 1867, not far from the modern value of 2760 K. In 1881, flame speed at the same mixture was measured as 2810 m/s.[8]

So far, only gaseous hydrogen has been discussed. Important to the application of hydrogen as a fuel are its properties as a liquid, which were not known until near the end of the nineteenth century.

Liquefaction of Gases through the Nineteenth Century

"The production of cold is a thing very worth of the inquisition both for the use and disclosure of causes," wrote Francis Bacon, the first systematic investigator of low temperature phenomena, in 1627.[9] Starting in the late eighteenth century, investigators sought to liquefy gases and reach lower and lower temperatures. By mid-nineteenth century, all but six of the known gases had been liquefied, and temperatures as low as 163 K had been attained by evaporating a mixture of ether and solid carbon dioxide. The six remaining gases were oxygen, nitrogen, nitric acid, carbon monoxide, methane, and hydrogen. (Helium, observed in the sun's gases in 1868, was not discovered on earth until 1895.)

In 1883, a Polish professor of physics, Zygmunt von Wroblewski, achieved the static liquefaction of oxygen and air. Thereafter, with the capability to cool compressed hydrogen to 73 K, efforts to liquefy it intensified. Wroblewski's attempt resulted in only a transient vapor. However, in 1885 he published some remarkably accurate physical data He gave hydrogen's critical temperature as 33 K (modern value, 33.3 K); critical pressure, 13.3 atmospheres (modern value, 12.8 atm); and boiling point, 23 K (modern value, 20.3 K).

Gas liquefaction techniques up to 1895 involved three basic steps: 1) compressing the gas to a high pressure, usually 50 atmospheres or more, 2) chilling the compressed gas to as low a temperature as possible using various cooling methods, and 3) expanding the chilled, compressed gas slowly from a high to a lower pressure by means of a needle valve. The cooling methods included, for example, evaporating an ether–solid carbon dioxide mixture or evaporating liquid ethylene, which Wroblewski used in liquefying oxygen. The third step made use of the Joule-Thomson effect for gases, based on experiments by Joule in 1845 and later refined by Thomson. They found that a gas, in slowly expanding from a high to a lower pressure, undergoes a change in temperature. The gas may be either heated or cooled by the expansion, depending upon the initial temperature and the particular gas. For most gases at room temperature, expansion results in cooling, as anyone who has used an aerosol can or operated a carbon dioxide fire extinguisher has experienced. Compressed air initially at 273 K, for example, will drop about ¼ K for each atmosphere drop in pressure, while carbon dioxide will drop 1½ K for each atmosphere drop in pressure. The temperature below which an expansion produces cooling is called the inversion temperature; it is high for most gases, but for hydrogen, it is about 193 K. Hydrogen, therefore, must be cooled below this temperature before it is expanded.

In 1895, a breakthrough occurred in gas liquefaction techniques, although it is not clear whether scientist or engineer first used it. The technique was to employ regenerative cooling in the liquefaction process, a simple concept in retrospect. Regenerative cooling means using a fluid as the coolant in a process in which the fluid is itself involved. In the liquefaction of gases, it means that the gas that is cooled by the Joule-Thomson expansion process is later used to cool the incoming compressed gas before expansion.

The regenerative cooling concept was an old idea, first introduced by Siemens in 1857 and used by Kirk, Coleman, Solvay, Linde, and others in refrigeration apparatus. In 1895, and within two weeks of each other, William Hampson in England and Carl

von Linde in Germany obtained patents for equipment to liquefy air using the Joule-Thomson expansion process and regenerative cooling.[10] Linde described his apparatus to physicists and chemists at Munich in 1895. A number of publications appeared that same year, among them one by James Dewar, English physicist and chemist, who described his apparatus for liquefying air using regenerative cooling.

Hampson's process for liquefying air was simple. He compressed air to 200 atmospheres, expanded it to one atmosphere, and passed the expanded, cooled air through a baffled heat exchanger to cool the incoming compressed air. His method was not very efficient, using power at a rate equivalent to 3.7 kilowatts to produce 1 liter per hour of liquid air. Hampson had his apparatus working at Brin's Oxygen Works by April 1896.[11]

Linde's approach was more complex than Hampson's, but it was also more efficient and suitable for large-scale production of liquid oxygen, nitrogen, and air. He used two stages of gas compression, precooled the air with a separate ammonia refrigeration system, and employed a coiled-tube heat exchanger having three concentric tubes for regenerative cooling. The heat exchanger was insulated by a wood case filled with wool.

Regenerative cooling proved to be the technological link needed to liquefy hydrogen. On 10 May 1898, James Dewar used it to become the first to statically liquefy hydrogen. Using liquid nitrogen he precooled gaseous hydrogen, under 180 atmospheres, then expanded it through a valve in an insulated vessel, also cooled by liquid nitrogen. The expanding hydrogen produced about 20 cubic centimeters of liquid hydrogen, about 1 percent of the hydrogen used.[12]

Dewar measured the density of liquid hydrogen at 0.07 kilogram per liter, the modern value, which is 1/14 the density of water and about 1/12 the density of kerosene or gasoline.

The insulated vessel Dewar used was the vacuum container flask he developed earlier which became known as "Dewar flasks," now simply dewars. His design was a very significant contribution to the storage and transportation of very cold liquefied gases such as oxygen, nitrogen, air, hydrogen, fluorine, and helium. Dewars are double-walled vessels with a vacuum in the annular space to minimize heat transfer by conduction and convection. The walls are silvered to reflect radiant heat. Following liquefaction of hydrogen, Dewar became very confident about storing and transporting it in his vacuum vessels, predicting that it could be handled as easily as liquid air. Dewar vessels, with engineering refinements, are used today to transport liquid hydrogen with very low loss rates.

By 1900, then, many of the major properties of gaseous and liquid hydrogen were known. Liquid air, oxygen, and nitrogen were being produced in quantity. Hydrogen had been liquefied, and dewar flasks made its storage and transportation feasible. Suggestions for using liquid hydrogen were not long in coming. The use of gaseous hydrogen for ballooning and its loss from venting brought a suggestion for using liquid hydrogen by storing and evaporating it in a double-walled bag.[13] Of greatest interest to our story, however, was a suggestion made by an obscure Russian schoolteacher, barely five years after Dewar's accomplishment, to use liquid hydrogen to fuel a space rocket.